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13. ABSTRACT (Maximum 200 words)  The original goal of this ASSERT research program was to extend our alternating-current thin-film electroluminescent (ACTFEL) device physics research in a new direction; namely, exploration of the potential of several classes of phosphor materials (trivalent oxides, nitrides, and oxynitrides) deposited by rf magnetron sputtering for ACTFEL thin-film display applications. This goal was modified to the exploration of certain divalent and trivalent nitrides such as CaSiN <sub>2</sub> :Eu and AlInN <sub>2</sub> :Tm for ACTFEL phosphor applications. This goal redirection is motivated by the perceived superior electron injection and transport properties of nitrides compared to oxides or oxynitrides. In order to achieve this goal, many modifications of the rf sputtering system and of the sputter target preparation system and handling procedure were undertaken. Additionally, a significant portion of the research effort was devoted to the development of high-quality insulators. The last phase of this research program was devoted to rf sputtering of ZnS:Tb phosphors in order to confirm that the sputter system is performing as desired and to test the viability of N acceptor doping as a means of improving the performance of sulfur-based ACTFEL phosphors.			
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**TRIVALENT PHOSPHORS FOR ACTFEL APPLICATIONS**

**Final Report**

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**9 July 1997**

**U. S. Army Research Center**

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**Oregon State University**

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# TRIVALENT PHOSPHORS FOR ACTFEL APPLICATIONS

## I. Statement of the Problem Studied

The original goal of this ASSERT research program was to extend our alternating-current thin-film electroluminescent (ACTFEL) device physics research in a new direction; namely, exploration of the potential of several classes of phosphor materials (trivalent oxides, nitrides, and oxynitrides) deposited by rf magnetron sputtering for ACTFEL thin-film display applications. This goal was modified to the exploration of certain divalent and trivalent nitrides such as  $\text{CaSiN}_2:\text{Eu}$  and  $\text{AlInN}_2:\text{Tm}$  for ACTFEL phosphor applications. This goal redirection is motivated by the perceived superior electron injection and transport properties of nitrides compared to oxides or oxynitrides. In order to achieve this goal, many modifications of the rf sputtering system and of the sputter target preparation system and handling procedure were undertaken. Additionally, a significant portion of the research effort was devoted to the development of high-quality insulators. The last phase of this research program was devoted to rf sputtering of  $\text{ZnS}:\text{Tb}$  phosphors in order to confirm that the sputter system is performing as desired and to test the viability of N acceptor doping as a means of improving the performance of sulfur-based ACTFEL phosphors.

## II. Summary of Important Results

### 1. Introduction

The original goal of this research program was to explore the potential of several classes of phosphor materials (trivalent oxides, nitrides, and oxynitrides) deposited by rf magnetron sputtering for alternating-current thin-film electroluminescent (ACTFEL) thin-film display applications. As this research project evolved, several issues became evident:

#1: It became clear that high-quality phosphor materials could not be deposited in our rf sputtering system unless the system was significantly modified. Therefore, several iterations of modifications to the rf sputtering system were undertaken. Many of these modifications were motivated by discussions with researchers at Planar America, Inc., Beaverton, Oregon who have very recently begun to aggressively employ sputtering in the development of new ACTFEL phosphors as a consequence of new insight into the nature of negative & positive ion effects in determining the quality of sputtered films and of their recent recognition of ways of minimize the deleterious effects associated with negative & positive ion bombardment.

#2: We have devoted a large amount of effort into improving our facilities for the preparation of sputter targets. At the beginning of this research program, we intended to purchase many of our sputter targets commercially. However, as the research program progressed, it became evident that in order to explore a wide range of materials and dopants, it was mandatory to prepare targets in-house. Moreover, according to researchers at the David Sarnoff Research Center, most commercially supplied targets are prepared in a manner such that killer centers are incorporated, so that such

targets are not appropriate for luminescent applications. Therefore, we have devoted much time and effort into improving our in-house target preparation facilities. Moreover, we have initiated a collaboration with Professor Arthur Sleight, an inorganic chemist at OSU who holds the Milton Harris Chair of Chemistry, devoted to the synthesis of rf sputter targets for the preparation of novel ACTFEL phosphors.

#3: As we attempted to fabricate our first ACTFEL devices, we came to appreciate the importance of high-quality insulators. Therefore, a substantial effort was devoted to developing high-quality insulators for ACTFEL fabrication.

#4: Our ASSERT work and our related ARO-supported ACTFEL device physics work led us to conclude that nitrides hold more promise for ACTFEL phosphor applications than do oxides or oxynitrides and that compensation & space charge effects play a crucially important role in the operation of ACTFEL devices. With this in mind, our current focus is to explore the intentional doping of ZnS:Tb by N in order to explore the viability of intentional defect engineering of a relatively well-known ACTFEL phosphor. Additionally, optimization of ZnS:Tb ACTFEL devices allows us to assess and improve our rf sputtering and ACTFEL fabrication procedures on a fairly well known material system prior to exploring more exotic materials systems. When this phase of the research is completed, we will investigate the viability of ternary nitride systems such as CaSiN<sub>2</sub>:Eu and AlInN<sub>2</sub>:Tm for ACTFEL phosphor applications.

The remaining sections of this Final Report summarize our work to date involving modification of the rf sputtering system, preparation of sputter targets, insulator development, phosphor deposition, and future work.

## 2. Modifications to the rf Sputtering System

In the early portion of this research program two major problems with our rf sputtering system were identified. The first problem involved oxygen contamination of nitride films. Helium leak detector analysis revealed that several very small oxygen leaks existed in the gas manifold. Several attempts to eliminate these leaks failed. Therefore, the gas manifold was completely redesigned, new mass flow controllers and valves were purchased and installed, and VCR fittings were substituted for Swagelock fittings. These modifications resolved the oxygen contamination problem, which is now monitored by a residual gas analyzer which has been permanently installed onto the rf sputtering system. The second problem was that "as deposited" films were amorphous; this is associated with the fact that our *in situ* heat was constrained to a maximum temperature of approximately 200° C. Modification of a viewport and O-rings allows us to attain temperatures of ~450-500° C so that the substrate heating problem is now resolved.

In a latter stage of this research program, at the suggestion of Dr. Sey-Shing Sun of Planar America, we replaced our 1" diameter sputter guns with 2" sputter guns. This change was motivated by Dr. Sun's observations that the low sputter rate, non-uniformity, and negative or positive ion effect problems inherent in the use of a 1" gun were undoubtedly contributing to some of the poor results that we had seen. Moreover, Dr. Sun provided us with plans for a redesign of the dark space

shield of our new 2" gun that minimize negative or positive ion effect problems . Installation of these new 2" guns required a system redesign and substantial machining in order to position the guns appropriately in front of the substrate holder.

### **3. Sputter Target Preparation Modifications**

The nonreactivity of N compared to O makes it very difficult to prepare pure nitrides that are free from oxygen contamination. Therefore, great care must be taken in the handling and preparation of nitride powders and targets in order to minimize oxygen contamination. To minimize oxygen contamination during target preparation, the following changes were made to our sputter target preparation procedure. First, all powders and targets are stored and transferred under vacuum using specially designed vacuum desiccators in which the vacuum is obtained using house vacuum and the integrity of the vacuum is insured via a vacuum pressure gauge attached to every vacuum desiccator. Second, all powder mixing and pressing are performed in a specially designed dry glove box under flowing nitrogen. Third, the sintering furnace has been entirely replumbed so that oxygen-free nitrogen or forming gas atmospheres can be maintained during sintering. One of the most important insights, resulting from the trip to the David Sarnoff Research Center, is that proper preparation of a sputter target involves several prolonged sintering treatments in which impurities are removed from the powder and target and during which the target is densified so that it is "as hard as a brick" (note that all of our early targets were subjected to very little, if any, sintering treatments and, thus, were soft and porous). Our current sintering procedure typically employs forming gas at moderate temperatures for the removal of oxygen and nitrogen annealing at elevated temperatures for nitridation and densification.

### **4. Insulator Development**

In order to fabricate an ACTFEL device, it is necessary to be able to deposit a high-quality insulator. Two types of insulators were investigated: (i) thick-film ceramic insulators with dielectric constants ~500-3,000 and breakdown strengths of ~0.1-1 MV/cm and (ii) thin-film insulators with dielectric constants of ~20-100 and breakdown strengths of ~1-3 MV/cm.

The thick-film ceramic insulators were investigated in collaboration with Northwest Microcircuits, Philomath, Oregon. ZnS:Mn ACTFEL devices on ceramic substrates with Au electrodes were successfully fabricated with dielectric constants of ~1600. Although this approach is promising, a significant amount of in-house development is required in order to optimize this approach, so that this approach was abandoned.

Thin-film dielectrics investigated included BaTa<sub>2</sub>O<sub>6</sub>, SrZr<sub>x</sub>Ti<sub>y</sub>O<sub>3</sub>, PbZr<sub>x</sub>Ti<sub>y</sub>O<sub>3</sub>, CaTiO<sub>3</sub>, Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub>. Ta<sub>2</sub>O<sub>5</sub> was found to be the best thin-film dielectric for our applications since it offered good dielectric properties (dielectric constants 23, breakdown strengths 1.5-3 MV/cm) and yet had an acceptable sputter rate (3 nm/min). However, the use of Ta<sub>2</sub>O<sub>5</sub> as an ACTFEL dielectric precludes the investigation of novel phosphors with extremely large threshold voltages (e.g. ~4-5 MV/cm) which do not possess space charge; although this limitation was originally considered to be important such that better insulators were thought to be necessary, our

recent understanding of the important role played by space charge leads us to feel that Ta<sub>2</sub>O<sub>5</sub> dielectrics are of adequate quality for our current purposes.

#### 4. Phosphor Deposition

In the first portion of this research program, the following novel phosphor materials were deposited: AlInN<sub>2</sub>, La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>:Tb, MgWO<sub>4</sub>, MgSiN<sub>2</sub>:Eu, Y<sub>2</sub>O<sub>3</sub>-WO<sub>3</sub>, In<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>, (Mg<sub>0.5</sub>Zn<sub>0.5</sub>)SiN<sub>2</sub>:Eu, ZnSiN<sub>2</sub>:Eu, and BaSiS<sub>4</sub>:Ce. All of the AlInN<sub>2</sub> layers deposited to date have significant oxygen contamination. La<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> was found to be difficult to anneal. MgWO<sub>4</sub> and In<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> were found to be conductive. All of the other phosphors were found to possess very little, if any, charge transfer. Of all of these materials, BaSiS<sub>4</sub>:Ce gave, by far, the best charge injection (as well as the highest brightness); note that this material, which showed the largest amount of charge transfer, is also the only material considered which has S as an anion constituent; we believe that materials which possess S anions very often have superior charge injection properties, possibly because of the tendency of these materials to possess S vacancies. However, a major problem is that it is very difficult to make a BaSiS<sub>4</sub> target, since this material is moisture-sensitive and these targets typically crumble or break during sputtering. For certain materials (e.g. In<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>:Tb), a Pd / Au injection layer was employed with some success in order to enhance the charge injection characteristics of the ACTFEL device; however, this approach does not seem to work for all materials. In summary, the primary difficulty that we have encountered in the fabrication of ACTFEL devices with novel phosphors is the lack of charge injection; this problem is encountered with every novel phosphor that we have investigated to date.

We believe that the charge injection problem encountered in the initial portion of this research program is primarily due to the poor stoichiometry and crystallinity of the deposited layers, but may also be associated with fundamental properties of the material itself. In order to improve the stoichiometry and crystallinity of the deposited layers, a significant effort was devoted to modifying the rf sputter system and target preparation procedure. Additionally, we are now collaborating with Professor Sleight's inorganic chemistry group in order to improve our target synthesis procedure.

We have identified two main materials properties of importance for obtaining efficient charge injection in ACTFEL phosphors. First, the electron effective mass of the phosphor should be small since charge injection by tunneling or phonon-assisted tunneling depends exponentially on the inverse of the effective mass. Although there is a very limited amount of data available, it appears that most nitrides have electron effective masses significantly smaller than that of oxides or oxynitrides. This would imply that oxides and oxynitrides will have large threshold voltages; this assertion seems to be consistent with the fact that all of the ACTFEL oxide phosphors reported in the literature to date require extremely large operating voltages.<sup>1,2</sup> Therefore, future studies will concentrate exclusively on nitrides as novel ACTFEL phosphors. Second, our recent ARO-sponsored ACTFEL device physics work points conclusively to the important role which space charge & charge compensation play in determining the performance of commercial ACTFEL phosphors such as ZnS and SrS. Therefore, novel ACTFEL phosphor future work will involve the assessment of space charge and, if necessary, defect engineering as a means of achieving the

appropriate compensation and space charge properties for efficient phosphor operation.

Current phosphor synthesis work is devoted to the optimization of sputtered ZnS:Tb ACTFEL devices. There are three primary driving forces motivating us to pursue this direction of research. First, optimization of a relatively well-studied ACTFEL materials system such as ZnS:Tb will allow us to confirm that our sputtering system is operating in an optimal manner. Second, we will explore the viability of employing defect engineering via N doping of the ZnS:Tb layer as a means of improving the efficiency of such ACTFEL devices. N doping is a means of accomodating the charge imbalance of the trivalent Tb atom when it substitutes for the divalent Zn atom via the addition of a N acceptor sitting on a S site. Third, if this defect engineering approach is successful in improving the brightness and aging stability of ZnS:Tb ACTFEL devices, this could lead to new monochrome or multi-color EL products;the poor brightness and stability of current state-of-the-art ZnS:Tb ACTFEL devices precludes commercial utilization.

## 5. Conclusions and Future Directions

This AASERT project has enabled us to extend our ACTFEL research activities beyond the device physics topics that we have previously pursued into the area of novel ACTFEL phosphor synthesis. Our work to date underscores the importance of properly preparing the sputter target so that it is stoichiometric and fully densified. Moreover, recognizing the importance of the synthesis of sputter targets has motivated us to initiate a collaboration with Professor Sleight, an inorganic chemist at OSU who holds the Milton Harris Chair of Chemistry, in order to improve our sputter target synthesis capability. Additionally, our initial work revealed inadequacies of our original rf sputtering system in terms of vacuum integrity, substrate temperature control, and the minimization of negative & positive ion effects. We have now eliminated these rf sputtering system problems. Our AASERT work, in conjunction with our ARO-supported device physics work, leads us to believe that nitrides are better ACTFEL phosphor candidates than oxides or oxynitrides since we expect nitrides to have smaller electron effective masses and better transport properties than comparable oxides or oxynitrides. In future work, we intend to work on the optimization of ternary nitrides such as CaSiN<sub>2</sub>:Eu and AlInN<sub>2</sub>:Tm for ACTFEL phosphor applications. However, prior to investigating these novel nitrides, we will conclude our investigation of the sputter deposition and N doping of ZnS:Tb ACTFEL devices in order to confirm that our sputtering system and ACTFEL fabrication procedure are optimal and to determine whether the performance of ZnS:Tb ACTFEL devices may be improved via N doping.

### **III. List of Participating Scientific Personnel**

1. Matthew Mueller
  - (i) M.S. Thesis: "Development and Characterization of AlInN as an Alternating-Current Thin-Film Electroluminescent Display Phosphor"
  - (ii) Currently employed at: Intel Corporation, Aloha, Oregon
2. Debra Walt
  - (i) Senior Project: "RF Sputtering of Alternating-Current Thin-Film Electroluminescent Insulators and Phosphors"
  - (ii) Currently: Rhodes Scholar, Oxford University, Great Britain
3. Wie- Ming Ang
  - (i) Ph.D. Thesis: "Novel ACTFEL Phosphors Deposited by RF Sputtering"
  - (ii) Currently employed at: Sharp Microelectronics Technology, Inc., Camas, Washington
4. Hieu Le
  - (i) M.S. Thesis: "RF Sputter Synthesis of ZnS:Tb,N ACTFEL Devices"
  - (ii) M. S. expected Summer 1997; has accepted a job at Intel Corporation, Aloha, Oregon
5. Paul D. Keir
  - (i) Ph.D. Thesis: "RF Sputter Synthesis of Novel ACTFEL Devices with Novel Phosphors"
  - (ii) Ph.D. expected Summer 1998
  - (iii) Currently supported on this project as an Intel Fellow

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